

PATENT SPECIFICATION

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(54) LONG TERM SILVER DIP

(71) We, J. GODDARD & SONS LIMITED,
a British Company of 15/35, Nelson Street,
Leicester, do hereby declare the invention for
which we pray that a patent may be granted
to us and the method by which it is to be
performed to be particularly described in and
by the following statement:—

The invention relates to a dip preparation for removing tarnish from a silver surface and imparting long term protection against further tarnish.

15 A dip preparation according to the invention comprises an acid which is stronger than hydrosulphuric acid but is not such as will in aqueous solution attack silver to any material extent, at least 1% by weight of a soluble compound capable of forming a soluble complex with silver ions which complex gives rise to substantially no silver ions in aqueous solution, and from 0.5% to 2% by weight of an organic compound containing an —SH group and capable of forming a transparent colourless protective layer on the silver surface.

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25 The complex-forming compound may be various substances examples of which are thiourea and thiosemicarbazide. Whether or not a given substance is suitable for this purpose may be ascertained by both of the following simple tests:—

30 1. A dilute solution, for example, 0.1% by weight of silver nitrate is prepared and is acidified with a strong acid, for example dilute sulphuric acid. A large excess over the silver nitrate of the compound to be tested
35 is added and hydrogen sulphide is bubbled

through: if no black precipitate is formed the compound is suitable.

40 2. Hydrogen sulphide is bubbled through an acidified solution of silver nitrate to produce a black precipitate of silver sulphide. Excess, over the silver nitrate, of the compound to be tested is then added: if the precipitate is dissolved the compound is suitable.

In both the above tests the amount of acid present must be in substantial excess of the amount of the compound being tested.

Since hydrosulphuric acid is a very weak acid (dissociation constant 9.1×10^{-8} at $180^{\circ}\text{C}.$) many acids may be used according to the invention. Examples of such acids are sulphuric, hydrochloric, phosphoric, acetic, citric and tartaric acids. The stronger the acid used the more rapid will be the detarnishing action. Conversely the stronger the acid the greater the degradation of the organic —SH group containing compound and the shorter the shelf life of the preparation. It will of course be understood that the acid must not be such that it will, in aqueous solution, attack silver to any material extent. The temperature at which the detarnishing operation is effected is of little practical importance but the higher the temperature the quicker will be the action.

The actual amount of silver sulphide present as tarnish is, in general small so that the total amount of complex-forming compound may also be small. With very small concentrations the action is unnecessarily slow, and thus at least 11.0% by weight of the complex forming compound should be present in the solution: in the case of thioruea we have found a concentration of from 1 to 5% by weight to be convenient. The preferred concentration of the acid in the solution is from 0.3 to 10% by weight. It will be understood that the weaker the acid used the larger will be the concentration required.

The proportion of organic —SH containing compound is important. Below 0.5% by weight the concentration is too low to give effective protection. Above 2% by weight the solute tends to be difficult to dissolve in most solvents and the cost of the preparation is unnecessarily increased.

Almost all organic compounds containing an $-\text{SH}$ group react with silver surfaces with the

formation of $-\text{S}\text{Ag}$ group. If the organic chain is long enough a protective monomolecular layer is formed. Some such layers are opaque and some are coloured but a number of compounds give satisfactory transparent colourless protective layers. The suitability of a particular compound can readily be determined by routine trial. Mercaptans and thioglycollates having at least 14 C atoms in the chain are satisfactory. C12 compounds tend to decompose after a short time and accelerate tarnishing. C18, C20 and C22 compounds are preferred. Up to C24 compounds have been tested and found effective. However we see no reason why compounds up to C 30 or even higher should not be useful according to the invention. Stearyl and cetyl mercaptans and thioglycollates are the best substances we know.

A dip preparation according to the invention is preferably made up in aqueous solution in which case a surfactant, usually a non-ionic or cationic emulsifying agent, is generally used in order to bring the organic $-\text{SH}$ containing compound into solution. Alternatively or in addition a co-solvent such as an alcohol, for example isopropyl alcohol may be used. If a large proportion of such co-solvent is used it may be possible to dispense with the surfactant. Suitable surfactants are ethylene-oxide condensates with aliphatic alcohols or phenols and ethoxylated long chain (C12-C18) aliphatic amines which are converted into salt form by the acid.

Silver surfaces suitable for treatment according to the invention include pure silver and silver alloys, such as the generally available sterling and Britannia silver, and plated silver surfaces. Impurities do not substantially affect the treatment which may of course be applied to an article only part of which has a silver surface, provided the remainder of the article is protected or inert to the treatment.

The wetting of the silver surface may be carried out by spraying or dipping. The invention includes both the dip preparation as hereinbefore defined suitable for use in the process of the invention, and the resulting treated articles.

Preferably the detarnishing is carried out in the presence of means for rendering the silver and any secondary metal associated therewith electrochemically negative during the detarnishing operation. Thus for example we are able to detarnish worn silver plate without any substantial discolouration of the worn areas. Furthermore the need to sort out articles containing metals other than silver may be avoided which obviously is of importance particularly where large amounts of silver have to be cleaned as in hotels and restaurants.

Thus the detarnishing process may be carried out in the presence of a metal which is more electropositive than the silver and any secondary metal associated therewith, such metal being in electrical contact with the silver article to form a cell. For example where copper is used as the metal support in silver plate, metals which are more electro-positive in the electrochemical series than copper can be used. It will be apparent that certain of such metals will be quite unsuitable as they will be too vigorously attacked by water or by the acid of the dip preparation. The metals which may be used can therefore be characterised as being those which are more electro-positive than the metal support and which are not attacked to any material extent by the dip preparation. Suitable metals where copper is the secondary metal are, for example, aluminium and nickel and where the secondary metal is iron or nickel, as in nickel silver, aluminium is satisfactory. Such metals may be present in the detarnishing process in any convenient form; thus the container in which the detarnishing process is carried out may be formed wholly or partly from them, or they may be introduced into the dip preparation before introduction of the silver articles to be cleaned, for example in the form of a plate, rod, turnings or filings; such metals in all cases being in electrical contact with the silver articles. The effect of incorporating such metals is that being more electropositive than the metal support, they attract the negatively charged ions and thus prevent discolouration of the metal support.

In one convenient method of operation, the dip preparation is placed in a container of suitable material, for example polyvinyl chloride or polyethylene, the silver articles to be cleaned are placed in an aluminium basket and the basket dipped in the solution. After removal from the dip preparation the basket may be dipped in water in order to rinse the silver.

In another method of operation the dip preparation is electrolysed, the article being treated forming the cathode. The container of the detarnishing solution may, for example, be formed from an electrical conductor and be connected as the anode; alternatively the anode may simply be introduced into the solution as a plate or rod. In this method of operation if the electrolysis is carried on too long, in general past the point when detarnishing is complete, a deposit may form on the silver, which is not however coherent and may be readily removed.

The invention is illustrated by the following Examples:

Example 1
2283 lb. of long term silver dip preparation are formulated as follows:

EXAMPLE 1

2283 lb. of long term silver dip preparation are formulated as follows:

Material	Quantity	% W/W of final solution
Water	190 gallons.	92.19
Thiourea	112 lbs.	4.90
Sulphuric Acid (S.G. 1.84)	2 Winchester	0.81
Hydrochloric Acid (S.G. 1.16)	1 Winchester	0.38
Active Emulsion	25 gallons.	
Dye solution	10 fl. ozs.	
Active Emulsion		
Water	41 gallons.	
Ethoxylated C12—C18 Aliphatic amine	4 gallons.	0.83
Stearyl Mercaptan	40 lbs.	0.88
Hydrochloric Acid (S.G. 1.16)	1 Winchester	
Dye Solution		
Solway Blue PFN 125	10 g.	0.001
ISO—Propyl Alcohol	5 fl. ozs	0.011
Water	5 fl. ozs	

EXAMPLE 2

Material	Quantity	% W/W of final solution
Water	190 galls.	92.19
Thiourea	112 lbs.	4.90
Phosphoric Acid (60%)	4 Winchester	1.1
Active Emulsion	25 galls.	
Dye Solution	10 fl. ozs.	
Active Emulsion		
Water	41 galls.	
Ethoxylated C12-C18 Aliphatic amine	4 gallons.	9.83
Stearyl Mercaptan	40 lbs.	0.88
Hydrochloric Acid (S.G. 1.16)	3 Winchester	
Dye Solution		
Solway Blue PBN 425	10 g.	9.091
ISO-Propyl Alcohol	5 fl. ozs	9.911
Water	5 fl. ozs	

WHAT WE CLAIM IS:—

1. A dip preparation for removing tarnish from a silver surface and imparting long term protection against further tarnish which comprises an acid which is stronger than hydrosulphuric acid but is not such as will in aqueous solution attack silver to any material extent, at least 1% by weight of a soluble compound capable of forming a soluble complex with silver ions which complex gives rise to substantially no silver ions in aqueous solution, and from 0.5% to 2% by weight of an organic compound containing an —SH group and capable of forming a transparent colourless protective layer on the silver surface.

2. A dip preparation according to claim 1 in which the complex-forming compound is thiourea or thiosemicarbazide.

3. A dip preparation according to claim 2 in which there is from 1 to 5% by weight of thiourea.

4. A dip preparation according to claims 1, 2 or 3 in which the acid is sulphuric acid and hydrochloric acid.

5. A dip preparation according to claims 1, 2, 3 or 4 in which the acid is phosphoric acid.

6. A dip preparation according to claims 1, 2, 3, 4 or 5 in which the concentration of the

acid is from 0.3 to 10% by weight of the preparation. 30

7. A dip preparation according to claims 1, 2, 3, 4, 5 or 6 in which the —SH containing compound is stearyl mercaptan. 35

8. A dip preparation according to claims 1, 2, 3, 4, 5 or 6 in which the —SH containing compound is cetyl mercaptan. 40

9. A dip preparation according to claims 1, 2, 3, 4, 5 or 6 in which the —SH containing compound is stearyl thioglycollate. 45

10. A dip preparation according to claims 1, 2, 3, 4, 5 or 6 in which the —SH containing compound is cetyl thioglycollate. 50

11. A dip preparation according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 which contains a non-ionic or cationic emulsifying agent. 45

12. A dip preparation according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 which contains an alcohol as a co-solvent. 55

13. A dip preparation substantially as herein described in Example 1.

14. A dip preparation substantially as herein described in Example 2.

15. A process for removing tarnish from a silver surface and imparting long term protection against further tarnish which comprises wetting the silver surface with a dip prepara-

tion according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14.

16. A process according to claim 15 in which the wetting is carried out by spraying or dipping.

17. A process according to claim 15 or claim 16 which is carried out in the presence of means for rendering the silver and any secondary metal associated therewith electrochemically negative during the detarnishing operation.

18. A process according to claim 17 in which the said means is a metal more electro-positive than the silver and any secondary metal associated therewith, such metal being in electrical contact with the silver article to form a cell.

19. A process according to claim 18 in which the more electropositive metal is aluminium.

20. A process according to claims 18 or 19 in which the dip preparation is placed in a container of polyvinyl chloride or polyethylene, the silver articles to be cleaned are placed in an aluminium basket and the basket dipped in the solution.

21. A process according to claim 17 in which the dip preparation is electrolysed, the article being treated forming the cathode.

22. A process according to claims 20 or 21 in which the articles are subsequently dipped in water in order to rinse the silver.

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